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(11) **EP 0 547 451 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
05.03.1997 Bulletin 1997/10

(51) Int. Cl.⁶: **C07D 213/61**, C07D 277/32,
C07D 261/10, A01N 43/40,
A01N 43/78, A01N 43/80

(21) Application number: 92120735.3

(22) Date of filing: 04.12.1992

(54) **Guanidine derivatives as insecticides**

Guanidinderivate als Insektizide

Dérivés de guanidine comme insecticides

(84) Designated Contracting States:
BE CH DE ES FR GB IT LI NL

(30) Priority: 17.12.1991 JP 352861/91

(43) Date of publication of application:
23.06.1993 Bulletin 1993/25

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(56) References cited:
EP-A- 0 254 859 **EP-A- 0 425 978**

Remarks:

The file contains technical information submitted
after the application was filed and not included in
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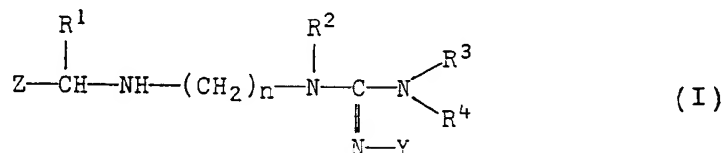
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Description

The present invention relates to novel guanidine derivatives, to a process for the preparation, and to their use as insecticides.

It has already been disclosed that a certain group of guanidine derivatives is useful as insecticides (see Japanese Laid-open patent application No. 10762/1988).

There have been found novel guanidine derivatives of the formula (I)



wherein

Z represents 2-chloro-5-pyridyl group, 2-chloro-5-thiazolyl group, or 3-chloro-5-isoxazolyl group,

R¹ represents hydrogen atom or C₁₋₄ alkyl group,

R² represents hydrogen atom, C₁₋₄ alkyl group, C₃₋₄ alkynyl group, C₃₋₄ alkenyl group or 2-chloro-5-pyridylmethyl,

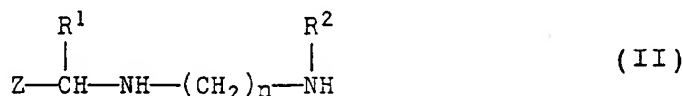
R³ and R⁴ each represent hydrogen atom, halogen atom, C₁₋₄ alkyl group, C₃₋₄ alkynyl group, C₃₋₄ alkenyl group, benzyl which may be substituted or a group represented by Z-C(R¹)H- wherein Z and R¹ are the same meanings as mentioned above,

n represents an integer of 2 or 3, and

Y represents nitro or cyano.

The guanidine derivatives of the formula (I) are obtained when

a) compounds of the following formula (II)



wherein Z, R¹, R² and n has the same meanings as mentioned above, are reacted with compounds of the formula (III)



wherein R³, R⁴ and Y have the same meanings as mentioned above, in the presence of inert solvents.

The novel guanidine derivatives of the formula (I) exhibit powerful insecticidal properties.

Surprisingly, the guanidine derivatives according to the invention exhibit a substantially greater insecticidal action than those known from the prior art of the above-mentioned Japanese Laid-open patent application.

Among the guanidine derivatives according to the invention, of the formula (I), preferred compounds are those in which

Z represents 2-chloro-5-pyridyl group or 2-chloro-5-thiazolyl group,

R¹ represents hydrogen atom or methyl group,

R² represents hydrogen atom, methyl group, allyl group, propargyl group or 2-chloro-5-pyridylmethyl,

R³ and R⁴ each represent hydrogen atom or methyl group,

Z	represents 2-chloro-5-pyridyl group or 2-chloro-5-thiazolyl group,
R ¹	represents hydrogen atom,
R ²	represents hydrogen atom or methyl group,
R ³ and R ⁴	each represent hydrogen atom,
n	represents an integer of 2 or 3, and
Y	represents nitro or cyano.

1-[2-(6-chloro-3-pyridylmethylamino)ethyl]-2-nitroguanidine,
1-[2-(6-chloro-3-pyridylmethylamino)propyl]-2-nitroguanidine, and
1-[2-(2-chloro-5-thiazolylmethylamino)ethyl]-2-nitroguanidine.

$$\text{Cl}-\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2 + \text{H}_3\text{CS}-\text{C}(\text{NH}_2)=\text{N}-\text{NO}_2 \xrightarrow{-\text{CH}_3\text{SH}} \text{Cl}-\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-\text{C}(\text{NH}_2)=\text{N}-\text{NO}_2$$

The starting materials of the formula (II) are known compounds disclosed by Japanese Laid-Open Patent application No.267561/1986 and 48680/1987, and the specific examples thereof may be mentioned:

N-(6-chloro-3-pyridylmethyl)-ethylene diamine,
N-(6-chloro-3-pyridylmethyl)-propylene diamine, and
N-(2-chloro-5-thiazolyl)-ethylene diamine.

The compounds of the formula (III) are well known in organic chemical field and, as the specific examples, there may be mentioned:

3-nitro-2-methylisothiourea, and
3-cyano-2-methylisothiourea.

Examples of such diluents are water; aliphatic, cycloaliphatic and aromatic, optionally chlorinated, hydrocarbons such as pentane, hexane, cyclohexane, petroleum ether, ligroin, benzene, toluene, xylene, dichloromethane, chloroform, carbon tetrachloride, ethylene chloride, chlorobenzene, dichlorobenzene, ethers such as diethyl ether, methyl ethyl ether, di-isopropyl ether, di-butyl ether, propylene oxide, dimethoxyethane (DME), dioxane, tetrahydrofuran (THF) and the like; nitriles such as acetonitrile, propionitrile, acrylonitrile, alcohols such as methanol, ethanol, iso-propanol,

butanol, ethylene glycol; esters such as ethyl acetate, amyl acetate; acid amides such as dimethyl formamide (DMF), diethyl acetamide (DMA), N-methylpyrrolidone, 1,3-dimethyl-2-imidazolidinone, hexamethylphosphoric triamide (HMPA); sulfones and sulfoxides such as dimethyl sulfoxide (DMSO), sulfolane; and, bases, for example, such as pyridine.

In the above mentioned process a), the reaction temperature can be varied within a substantially wide range. In general, the reaction is carried out at a temperature of from -20 °C to 100 °C, preferably from 10 °C to 80 °C.

Further, the reaction is carried out under normal pressure, although it is also possible to employ a higher or reduced pressure.

When the above mentioned process a) according to the present invention is carried out, use is made, for example, of the above mentioned compound (III) in the amount from 1.0 to 1.5 mols, preferably 1.0 to 1.1 mols, per one mol of the above mentioned compound (II), optionally in the presence of inert solvents such as water, for example, to obtain the desired compounds of the formula (I).

The active compounds of the formula (I) are well tolerated by plants, have a favorable level of toxicity to warm-blooded animals, and can be used for combating arthropod pests, especially insects which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development. The above-mentioned pests include:

from the class of the *Isopoda*, for example, *Oniscus Asellus*, *Armadillidium vulgare* and *Porcellio scaber*;
 from the class of the *Diplopoda*, for example, *Blaniulus guttulatus*;
 from the class of the *Chilopoda*, for example, *Geophilus carpophagus* and *Scutigera spec.*;
 from the class of the *Symphyla*, for example, *Scutigera immaculata*;
 from the order of the *Thysanura*, for example, *Lepisma saccharina*;
 from the order of the *Collembola*, for example, *Onychiurus armatus*;
 from the order of the *Orthoptera*; for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*, *Acheta domesticus*, *Gryllotalpa spp.*, *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*;
 from the order of the *Dermaptera*, for example, *Forficula auricularia*;
 from the order of the *Isoptera*, for example, *Reticulitermes spp.*;
 from the order of the *Anoplura*, for example, *Phylloxera vastatrix*, *Pemphigus spp.*, *Pediculus humanus corporis*, *Haematopinus spp.* and *Linognathus spp.*;
 from the order of the *Mallophaga*, for example, *Trichodectes spp.* and *Damalinea spp.*;
 from the order of the *Thysanoptera*, for example, *Hercinothrips femoralis* and *Thrips tabaci*,
 from the order of the *Heteroptera*, for example, *Eurygaster spp.*, *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma spp.*;
 from the order of the *Homoptera*, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Aphis fabae*, *Doralis pomi*, *Eriosoma lanigerum*, *Hyalopteris arundinis*, *Macrosiphum avenae*, *Myzus spp.*, *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca spp.*, *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus spp.* and *Psylla spp.*;
 from the order of the *Lepidoptera*, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plubella maculipennis*, *Malacosoma neustria*, *Euprocitis chrysorrhoea*, *Lymantria spp.*, *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis spp.*, *Euxoa spp.*, *Feltia spp.*, *Earias insulana*, *Heliothis spp.*, *Spodoptera exigua*, *Mamestra brassicae*, *Panolis flammea*, *Prodenia litura*, *Spodoptera spp.*, *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris spp.*, *Chilo spp.*, *Pyrausta nubilalis*, *Ephesia kuehniella*, *Galleria mellonella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysia ambiguella*, *Homona magnanima* and *Tortrix viridana*;
 from the order of the *Coleoptera*, for example, *Anobium punctatum*, *Rhizophthera dominica*, *Acanthoscelides obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica spp.*, *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria spp.*, *Oryzaephilus surinamensis*, *Anthonomus spp.*, *Sitophilus spp.*, *Otiorynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes spp.*, *Trogoderma spp.*, *Anthrenus spp.*, *Athagenus spp.*, *Lyctus spp.*, *Meligethes aeneus*, *Ptinus spp.*, *Niptus hololeucus*, *Gibbium psyllioides*, *Tribolium spp.*, *Tenebrio molitor*, *Agriotes spp.*, *Conoderus spp.*, *Melolontha*, *Amphimallon solstitialis* and *Costelytra zealandica*;
 from the order of the *Hymenoptera* for example, *Diprion spp.*, *Hoplocampa spp.*, *Lasius spp.*, *Monomorium pharaonis* and *Vespa spp.*;
 from the order of the *Diptera*, for example, *Aedes spp.*, *Anopheles spp.*, *Culex spp.*, *Drosophila melanogaster*, *Musca spp.*, *Fannia spp.*, *Calliphora erythrocephala*, *Lucilia spp.*, *Chrysomyia spp.*, *Cuterebra spp.*, *Gastrophilus spp.*, *Hyppobosca spp.*, *Stomoxys spp.*, *Oestrus spp.*, *Hypoderma spp.*, *Tabanus spp.*, *Tannia spp.*, *Bibio*

hortulanus, *Oscinella frit*, *Phorbia* spp., *Pegomyia hyoscyami*, *Ceratitis capitata*, *Dacus oleae* and *Tipula paludosa*.

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances, coating compositions for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans and fumigating coils, as well as ULV cold mist and warm mist formulations.

These formulations may be produced in known manner, for example by mixing the active compounds with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid solvents diluents or carriers, there are suitable in the main, aromatic hydrocarbons, such as xylene, toluene or alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethylformamide and dimethylsulphoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid carriers there may be used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates. As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysis products.

Dispersing agents include, for example, lignin sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or lattices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulation.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent by weight.

The active compounds according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, baits, sterilizing agents, acaricides, nematocides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas, substances produced by microorganisms.

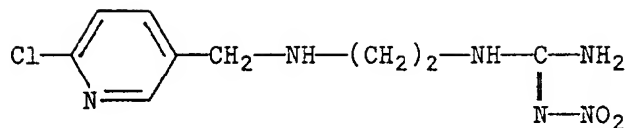
The active compounds according to the invention can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergistic agents. Synergistic agent are compounds which increase the action of the active compounds, without it being necessary for the synergistic agent added to be active itself.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 100% by weight of active compound, preferably between 0.0001 and 1% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay as well as a good stability to alkali on limed substrates.

The preparation and use of the active compounds according to the invention can be seen from the following examples.

Example 1

A mixture consisting of N-(6-chloro-3-pyridylmethyl) ethylenediamine (3.7 g), 3-nitro-2-methylisothiurea (2.7 g) and ethanol (20 ml) was stirred at 30 °C until methylmercaptan ceased to be generated therefrom. After cooling, the separated crystals were taken out under filtration, to obtain the desired 1-[2-(6-chloro-3-pyridyl-methylamino)ethyl]-2-nitro-guanidine.

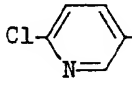
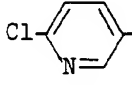
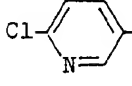
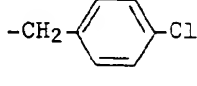
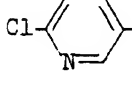
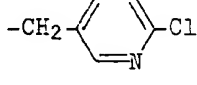
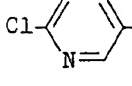
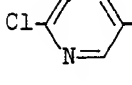
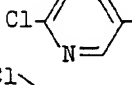
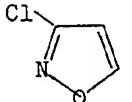
mp 119-122 °C

According to the same way as those employed in the above-mentioned Example, a number of compounds can be obtained as specifically shown in Table 1, wherein the compounds prepared in the aforementioned-Example is also shown.

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Table 1 (continued)

Comp. No.	Z	R ¹	R ²	R ³	R ⁴	Y	n	Melting point (°C)
10		H	i-Pr	H	H	NO ₂	2	
11		H	t-Bu	H	H	NO ₂	2	
12		H		H	H	NO ₂	2	
13		H		H	H	NO ₂	2	
14		H	-CH ₂ -CH=CH ₂	H	H	NO ₂	2	
15		H	-CH ₂ -C≡CH	H	H	NO ₂	2	
16		H	-CH ₂ -C≡CH	H	H	NO ₂	3	
17*		H	H	H	H	NO ₂	2	

* not part of claimed invention

Biotest Example:Example 2

- 5 Biotest carried out against *Nephotettix cincticeps* [green rice leafhopper] exhibiting resistance to organophosphorus and carbamate series insecticides

Preparation of test formulation:

- 10 solvent: 3 parts by weight of xylene
Emulsifier: 1 part by weight of polyoxyethylenealkylphenyl-ether

- To prepare suitable formulations of the active compounds, 1 part by weight of each of the active compounds was mixed with the above-mentioned amount of the solvent containing the above-mentioned amount of the emulsifier, and
15 the mixture was diluted with water to the predetermined concentration.

Test Method:

- Use was made of a plurality of pots each having a diameter of 12 cm in which were planted rice plant seedlings each
20 having a height of about 10 cm.
Onto each of the potted rice-plant seedling sprayed 10 ml of an aqueous solution of the active compound as prepared in the above and having the predetermined concentration. After the spread solution was dried up, each of the pots was covered with a metallic net having a diameter of 7 cm and height of 14 cm, in which 30 head of female adults of *Nephotettix cincticeps* exhibiting resistance to organophosphorus and carbamate series insecticides were released, and then
25 each pot was placed in a constant temperature chamber. After two days, the number of the killed insects was determined to obtain the mortality of insects.

Example 3

- 30 Test on planthoppers exhibiting resistance to organophosphorus and carbamate series insecticides

Test Method:

- Use was made of a plurality of pots each having a diameter of 12 cm in which were planted rice plant seedlings
35 each having a height of about 10 cm.
Onto each of the potted rice-plant seedlings was spread 10 ml of an aqueous solution of the active compound having the predetermined concentration which had been prepared in the manner similar to the above-mentioned Example 2. After the thus spread solution was dried up, each pot was covered with a metallic net having a diameter of 7 cm and a height of 14 cm, into which were released 30 head of female adults of brown planthoppers (*Nilaparvata lugens*) exhibiting resistance to organophosphorus and carbamate-series insecticides, and then each pot was placed in a constant
40 temperature chamber. After two days, the number of the killed insects was determined to obtain the mortality of insects.

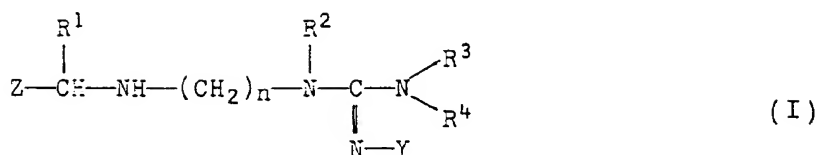
In the manner similar to the method mentioned above, mortality was determined each on Sezirounka (white-backed planthopper, *Sogatella furcifera*) and Himetobiunka (smaller blown planthopper, *Laodelphax striatellus*) having resistance to organophosphoric pesticides.

- 45 In the above-mentioned Test Examples 2 and 3, use was made, as the representative example of the active compounds represented by the formula (I), of the compounds indicated by 1, 2 and 3 in the Table 1 with effective controlling effects exhibiting on each of the noxious insects, for example, a 100% control at a dosage of 200 ppm.

Claims

- 50 1. Guanidine derivatives of the formula (I)

55



wherein

- Z represents 2-chloro-5-pyridyl group, 2-chloro-5-thiazolyl group,
 R¹ represents hydrogen atom or C₁₋₄ alkyl group,
 R² represents hydrogen atom, C₁₋₄ alkyl group, C₃₋₄ alkynyl group, C₃₋₄ alkenyl group or 2-chloro-5-pyridyl-methyl,
 R³ represents hydrogen atom, halogen atom, C₁₋₄ alkyl group, C₃₋₄ alkynyl group, C₃₋₄ alkenyl group, benzyl which may be substituted or a group represented by Z-C(R¹)H- wherein Z and R¹ are the same meaning of the above,
 R⁴ represents hydrogen atom, halogen atom, C₁₋₄ alkyl group, C₃₋₄ alkynyl group, C₃₋₄ alkenyl group, benzyl which may be substituted or a group represented by Z-C(R¹)H- wherein Z and R¹ are the same meaning of the above,
 n represents an integer of 2 or 3, and
 Y represents nitro or cyano.

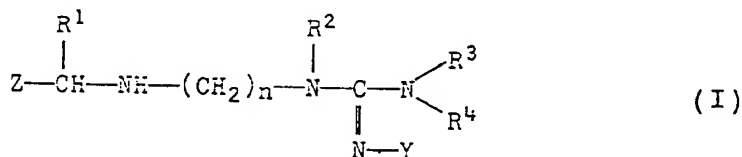
2. The compounds of the claim 1 wherein

- Z represents 2-chloro-5-pyridyl group or 2-chloro-5-thiazolyl group,
 R¹ represents hydrogen atom or methyl group,
 R² represents hydrogen atom, methyl group, allyl group, propargyl group or 2-chloro-5-pyridylmethyl,
 R³ represents hydrogen atom or methyl group,
 R⁴ represents hydrogen atom or methyl group,
 n represents an integer of 2 or 3, and
 Y represents nitro or cyano.

3. The compounds of the claim 1 wherein

- Z represents 2-chloro-5-pyridyl group or 2-chloro-5-thiazolyl group,
 R¹ represents hydrogen atom,
 R² represents hydrogen atom or methyl group,
 R³ represents hydrogen atom,
 R⁴ represents hydrogen atom,
 n represents an integer of 2 or 3, and
 Y represents nitro or cyano.

4. Process for the preparation of guanidine derivatives of the formula (I) according to claim 1



wherein

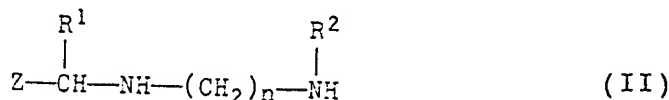
- Z represents 2-chloro-5-pyridyl group, 2-chloro-5-thiazolyl group,
 R¹ represents hydrogen atom or C₁₋₄ alkyl group,
 R² represents hydrogen atom, C₁₋₄ alkyl group, C₃₋₄ alkynyl group, C₃₋₄ alkenyl group or 2-chloro-5-pyridylmethyl,

R^3 and R^4 each represent hydrogen atom, halogen atom, C_{1-4} alkyl group, C_{3-4} alkynyl group, C_{3-4} alkenyl group, benzyl which may be substituted or a group represented by $Z-C(R^1)H$ - wherein Z and R^1 are the same meanings as mentioned above,

n represents an integer of 2 or 3, and

Y represents nitro or cyano,

characterized in that compounds of the following formula (II)



wherein Z, R^1 , R^2 and n have the same meanings as mentioned above, are reacted with compounds of the formula (III)

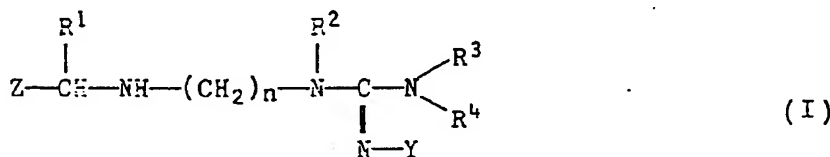


wherein R^3 , R^4 and Y have the same meanings as mentioned above, in the presence of inert solvents.

5. Insecticidal compositions, characterized in that they contain at least one guanidine derivative of the formula (I) according to claim 1.
6. Process of combating insect, characterized in that guanidine derivatives of the formula (I) according to claim 1 are allied to act on insect and/or their habitat.
7. Use of guanidine derivatives of the formula (I) according to claim 1 for combating insect.
8. Process for the preparation of insecticidal compositions, characterized in that guanidine derivatives of the formula (I) according to claim 1 are mixed with extenders and/or surface active agents.

Patentansprüche

1. Guanidinderivate der Formel (I)



wobei

Z eine 2-Chlor-5-pyridylgruppe oder 2-Chlor-5-thiazolylgruppe bedeutet,

R^1 ein Wasserstoffatom oder eine C_{1-4} -Alkylgruppe bedeutet,

R^2 ein Wasserstoffatom, eine C_{1-4} -Alkylgruppe, C_{3-4} -Alkynylgruppe, C_{3-4} -Alkenylgruppe oder 2-Chlor-5-pyridylmethyl bedeutet,

R^3 ein Wasserstoffatom, Halogenatom, eine C_{1-4} -Alkylgruppe, C_{3-4} -Alkynylgruppe, C_{3-4} -Alkenylgruppe, Benzyl, das substituiert sein kann, oder eine Gruppe, die durch $Z-C(R^1)H$ - dargestellt wird, wobei Z und R^1 dasselbe wie oben bedeuten, bedeutet,

R^4 ein Wasserstoffatom, Halogenatom, eine C_{1-4} -Alkylgruppe, C_{3-4} -Alkynylgruppe, C_{3-4} -Alkenylgruppe,

Benzyl, das substituiert sein kann, oder eine Gruppe, die durch $Z-C(R^1)H$ - dargestellt wird, wobei Z und R^1 dasselbe wie oben bedeuten, bedeutet,
n eine der ganzen Zahlen 2 oder 3 bedeutet und
Y Nitro oder Cyano bedeutet.

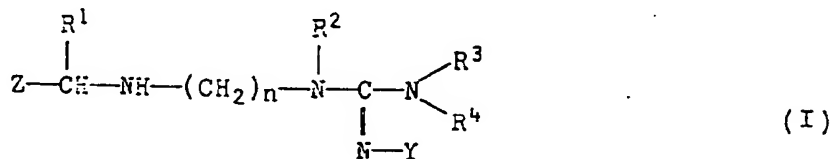
2. Verbindungen gemäß Anspruch 1, wobei

Z eine 2-Chlor-5-pyridylgruppe oder 2-Chlor-5-thiazolylgruppe bedeutet,
 R^1 ein Wasserstoffatom oder eine Methylgruppe bedeutet,
 R^2 ein Wasserstoffatom, eine Methylgruppe, Allylgruppe, Propargylgruppe oder 2-Chlor-5-pyridylmethyl bedeutet,
 R^3 ein Wasserstoffatom oder eine Methylgruppe bedeutet,
 R^4 ein Wasserstoffatom oder eine Methylgruppe bedeutet,
n eine der ganzen Zahlen 2 oder 3 bedeutet und
Y Nitro oder Cyano bedeutet.

3. Verbindungen gemäß Anspruch 1, wobei

Z eine 2-Chlor-5-pyridylgruppe der 2-Chlor-5-thiazolylgruppe bedeutet,
 R^1 ein Wasserstoffatom bedeutet,
 R^2 ein Wasserstoffatom oder eine Methylgruppe bedeutet,
 R^3 ein Wasserstoffatom bedeutet,
 R^4 ein Wasserstoffatom bedeutet,
n eine der ganzen Zahlen 2 oder 3 bedeutet und
Y Nitro oder Cyano bedeutet.

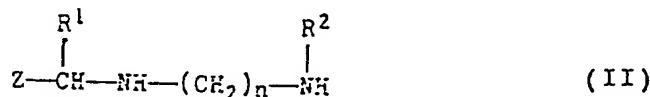
4. Verfahren zur Herstellung von Guanidinderivaten der Formel (I) gemäß Anspruch 1



wobei

Z eine 2-Chlor-5-pyridylgruppe oder 2-Chlor-5-thiazolylgruppe bedeutet,
 R^1 ein Wasserstoffatom oder eine C_{1-4} -Alkylgruppe bedeutet,
 R^2 ein Wasserstoffatom, eine C_{1-4} -Alkylgruppe, C_{3-4} -Alkylgruppe, C_{3-4} -Alkenylgruppe oder 2-Chlor-5-pyridylmethyl bedeutet,
 R^3 und R^4 jeweils ein Wasserstoffatom, Halogenatom, eine C_{1-4} -Alkylgruppe, C_{3-4} -Alkylgruppe, C_{3-4} -Alkenylgruppe, Benzyl, das substituiert sein kann, oder eine Gruppe, die durch $Z-C(R^1)H$ - dargestellt wird, wobei Z und R^1 dasselbe wie oben bedeuten, bedeuten,
n eine der ganzen Zahlen 2 oder 3 bedeutet und
Y Nitro oder Cyano bedeutet,

dadurch gekennzeichnet, daß Verbindungen der folgenden Formel (II)



wobei Z, R^1 , R^2 und n dasselbe wie oben bedeuten, in Gegenwart inerter Lösungsmittel mit Verbindungen der Formel (III)

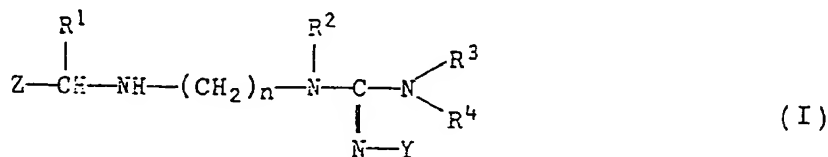


wobei R^3 , R^4 und Y dasselbe wie oben bedeuten, umgesetzt werden.

5. Insektizide Zusammensetzungen, dadurch gekennzeichnet, daß sie wenigstens ein Guanidinderivat der Formel (I) gemäß Anspruch 1 enthalten.
6. Verfahren zur Bekämpfung von Insekten, dadurch gekennzeichnet, daß man Guanidinderivate der Formel (I) gemäß Anspruch 1 auf Insekten und/oder ihren Lebensraum einwirken läßt.
7. Verwendung von Guanidinderivaten der Formel (I) gemäß Anspruch 1 zur Bekämpfung von Insekten.
8. Verfahren zur Herstellung insektizider Zusammensetzungen, dadurch gekennzeichnet, daß Guanidinderivate der Formel (I) gemäß Anspruch 1 mit Streckmitteln und/oder Tensiden gemischt werden.

Revendications

1. Dérivés de guanidine de formule (I)



dans laquelle

- | | |
|--------------|---|
| Z | représente un groupe 2-chloro-5-pyridyle, un groupe 2-chloro-5-thiazolyle ou 3-chloro-5-isoxazolyle, |
| R^1 | représente un atome d'hydrogène ou un groupe alkyle en C_1 à C_4 , |
| R^2 | représente un atome d'hydrogène, un groupe alkyle en C_1 à C_4 , un groupe alcynyle en C_3 ou C_4 , un groupe alcényle en C_3 ou C_4 ou un groupe 2-chloro-5-pyridylméthyle, |
| R^3 | représente un atome d'hydrogène, un atome d'halogène, un groupe alkyle en C_1 à C_4 , un groupe alcynyle en C_3 ou C_4 , un groupe alcényle en C_3 ou C_4 , un groupe benzyle qui peut être substitué ou un groupe représenté par la formule $\text{Z}-\text{C}(\text{R}^1)\text{H}$ - dans laquelle Z et R^1 répondent aux définitions précitées, |
| R^4 | représente un atome d'hydrogène, un atome d'halogène, un groupe alkyle en C_1 à C_4 , un groupe alcynyle en C_3 ou C_4 , un groupe alcényle en C_3 ou C_4 , un groupe benzyle qui peut être substitué ou un groupe représenté par la formule $\text{Z}-\text{C}(\text{R}^1)\text{H}$ - dans laquelle Z et R^1 répondent aux définitions précitées, |
| n | représente le nombre entier 2 ou 3, et |
| Y | représente un groupe nitro ou cyano. |

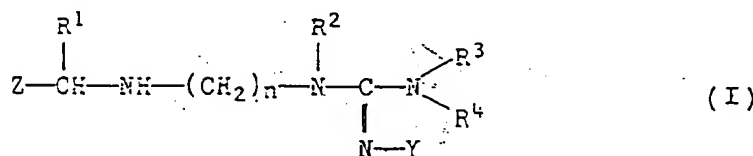
2. Composés suivant la revendication 1, dans lesquels

- | | |
|--------------|--|
| Z | représente un groupe 2-chloro-5-pyridyle ou 2-chloro-5-thiazolyle, |
| R^1 | représente un atome d'hydrogène ou un groupe méthyle, |
| R^2 | représente un atome d'hydrogène, un groupe méthyle, un groupe allyle, un groupe propargyle ou un groupe 2-chloro-5-pyridylméthyle, |
| R^3 | représente un atome d'hydrogène ou un groupe méthyle, |
| R^4 | représente un atome d'hydrogène ou un groupe méthyle, |
| n | représente le nombre entier 2 ou 3, et |
| Y | représente un groupe nitro ou cyano. |

3. Composés suivant la revendication 1, dans lesquels

- Z représente un groupe 2-chloro-5-pyridyle ou un groupe 2-chloro-5-thiazolyle,
 R¹ représente un atome d'hydrogène,
 R² représente un atome d'hydrogène ou un groupe méthyle,
 R³ représente un atome d'hydrogène,
 R⁴ représente un atome d'hydrogène,
 n représente le nombre entier 2 ou 3, et
 Y représente un groupe nitro ou cyano.

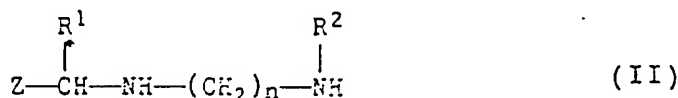
4. Procédé pour la préparation de dérivés de guanidine de formule (I) suivant la revendication 1



formule dans laquelle Z représente un groupe 2-chloro-5-pyridyle, un groupe 2-chloro-5-thiazolyle ou un groupe 3-chloro-5-isoxazolyle,

- R¹ représente un atome d'hydrogène ou un groupe alkyle en C₁ à C₄,
 R² représente un atome d'hydrogène, un groupe alkyle en C₁ à C₄, un groupe alcynyle en C₃ ou C₄,
 un groupe alcényle en C₃ ou C₄ ou un groupe 2-chloro-5-pyridylméthyle,
 R³ et R⁴ représentent chacun un atome d'hydrogène, un atome d'halogène, un groupe alkyle en C₁ à C₄,
 un groupe alcynyle en C₃ ou C₄, un groupe alcényle en C₃ ou C₄, un groupe benzyle qui peut être
 substitué ou un groupe représenté par la formule Z-C(R¹)H- dans laquelle Z et R¹ répondent aux
 définitions précitées,
 n représente le nombre entier 2 ou 3, et
 Y représente un groupe nitro ou cyano,

caractérisé en ce que des composés répondant à la formule (II) suivante



dans laquelle Z, R¹, R² et n répondent aux définitions précitées,
 sont amenés à réagir avec des composés de formule (III)



dans laquelle R³, R⁴ et Y répondent aux définitions précitées,
 en présence de solvants inertes.

5. Compositions insecticides, caractérisées en ce qu'elles contiennent au moins un dérivé de guanidine de formule (I) suivant la revendication 1.
6. Procédé pour combattre des insectes, caractérisé en ce que des dérivés de guanidine de formule (I) suivant la revendication 1 sont amenés à agir sur des insectes et/ou leur habitat.
7. Utilisation de dérivés de guanidine de formule (I) suivant la revendication 1, pour combattre des insectes.

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8. Procédé pour la préparation de compositions insecticides, caractérisé en ce que des dérivés de guanidine de formule (I) suivant la revendication 1 sont mélangés à des diluants et/ou des agents tensio-actifs.

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